THE STRUCTURE OF THE CARBOXYL GROUP. I. THE INVESTIGATION OF FORMIC ACID BY THE DIFFRACTION OF ELECTRONS

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The electronic structure of a carboxylic acid has been ordinarily written as $R:C:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H$. It has been recognized,[1] however, that the structure $R:C::O^{+}:H$ also may make a significant contribution to the normal state of the molecule, and the existence of such resonance of the double bond between the two oxygen atoms has been supported by thermochemical data,[2] the resonance energy being 1.20 v. e. for the carboxyl group in acids and in esters. During the investigation reported in this paper we have verified the resonating structure by the determination of interatomic distances in formic acid, and have also shown that in the dimer of formic acid the molecules are joined together by hydrogen bonds between the oxygen atoms of the carboxyl groups.

Formic acid was prepared by passing dry hydrogen sulfide over the copper salt and was purified by the method of A. S. Coolidge.[3] For this preparation we are indebted to Mr. John Y. Beach. Electron-diffraction photographs were made in the manner previously described.[4] The gas was at a pressure of about 110 mm., the vapor pressure of the liquid at 45°C. The electron wave-lengths used were about 0.061 Å, as determined by calibration of the apparatus with gold foil, for which the value $a_0 = 4.070$ Å was assumed. The film was 12.19 cm. from the gas nozzle.

Measured values of $4\pi \sin \frac{\theta}{2}/\lambda$ for five maxima and four minima (averaged for seven photographs) are given in table 1. The qualitative appearance of the photographs corresponds to the following description. The first maximum is weak. The second is strong and sharp, with a shelf on the outer side, causing the third minimum to be displaced outward. The third and fourth maxima lie close together, and are of about equal apparent intensity. They are followed by a sharp fifth minimum and fifth maximum.

A previous study of formic acid has been made by Hengstenberg and Brú,[5] who report their photographs to show three rings. Their measured

diameter is given for only one ring, their value $4\pi \sin \frac{\theta}{2}/\lambda = 5.96 \pm 0.1$ agreeing reasonably well with our value for the second maximum. They ascribed a structure to the double molecules of formic acid which we are unable to accept. This structure results from placing the O–C–O angle in the carboxyl group equal to 125°, and orienting two molecules HCOOH in such a way that the four oxygen atoms form a regular tetrahedron. The simple intensity curve

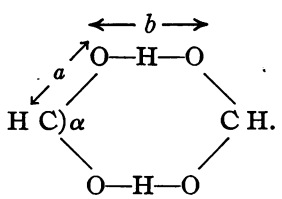
$$I = \sum_i \sum_j Z_i Z_j \frac{\sin x_{ij}}{x_{ij}}$$

with

$$x_{ij} = 4\pi l_{ij} \frac{\sin \frac{\theta}{2}}{\lambda}$$

calculated for this model is shown as Curve *A* of figure 1. It is not at all compatible even with the qualitative appearance of our photographs. (The curve given by Hengstenberg and Brú on page 357 of their paper is also not compatible with our photographs. This curve differs slightly from Curve *A*, apparently because of their neglect of the carbon-oxygen and carbon-carbon terms between the two carboxyl groups.)

In formulating possible structures for the double molecules for comparison with our photographs, we have made use of the idea, first suggested by Latimer and Rodebush,[6] that the carboxylic acids form dimers as a result of the formation of hydrogen bonds between the oxygen atoms of the two carboxyl groups, the structure of the double molecule being



Such a structure would place all of the atoms in the same plane. It would be especially stable because of the equivalence of the two oxygen atoms, permitting complete resonance of the double bond (as in the ion). For the distances *a* and *b* and the angle α we selected the following values for trial:

Model *B:*	α = 135°	*a* = 1.28 Å	*b* = 2.65 Å
C:	125°	1.28	2.50
D:	125°	1.28	2.65
E:	125°	1.28	2.75
F:	120°	1.28	2.65

The calculated intensity curves (two of which are given in figure 1) are not those for the double molecules alone, but for an equilibrium mixture[3] of 85% (by weight) of $(HCOOH)_2$ and 15% of HCOOH; these curves differ only very slightly from the curves for pure $(HCOOH)_2$. The value $a = 1.28$ Å is the sum of the double-bond radii for carbon and oxygen. The curves are applicable to any models with the same ratios of b/a.

Comparison with the description of the photographs given above shows that Curve D is in excellent qualitative agreement with the photographs, even such features as the shelf on the second maximum and the sharpness

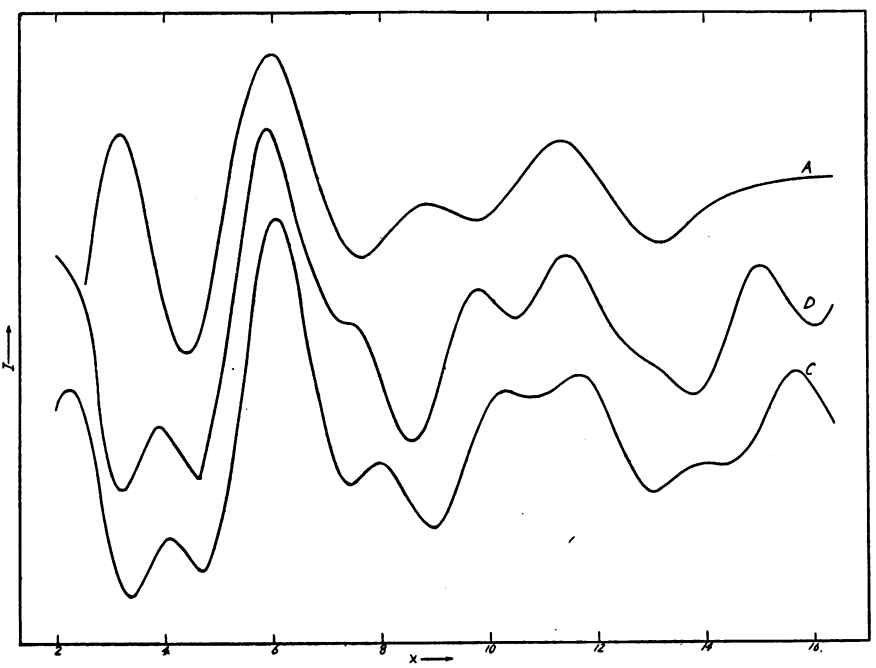


FIGURE 1

Calculated intensity curves for models A, C and D of formic acid as functions of $x = 4\pi \sin\frac{\theta}{2}/\lambda$.

of the fifth minimum being reproduced. Curves B and C, while somewhat similar to Curve D and to the photographs, show sufficiently pronounced qualitative deviations from the photograph to eliminate the corresponding models. Thus Curve B shows only a single maximum in a region where two (the third and fourth) are observed, and Curve C shows an additional maximum near the third minimum and a small maximum just where the sharp fifth minimum is observed. Curves E and F are somewhat inferior to D in that the shelf on the outer side is not as pronounced as indicated by the photographs, and the quantitative agree-

ment is also somewhat inferior. We conclude that the structure of $(HCOOH)_2$ is closely represented by Model *D*, and does not differ from this model to as great an extent as is indicated by Models *B*, *C*, *E* and *F*.

TABLE 1

MAXIMUM	MINIMUM	$\frac{4\pi \sin \theta/2}{\lambda}$ OBSERVED	x CALCULATED FOR CURVE *D*	O–H–O DISTANCE CALCULATED FOR *D*	*B*	*C*	*E*	*F*
1		3.95	3.97	2.67 Å	2.68 Å	2.61 Å	2.69 Å	2.65 Å
	2	(4.86)						
2		5.79	5.92	2.71	2.70	2.62	2.75	2.65
	3	8.52	8.58	2.67	2.70	2.63	2.72	2.65
3		9.48	9.78	2.73		2.72	2.79	2.75
	4	10.63	10.50	2.62		2.57	2.65	2.64
4		11.72	11.45	2.59		2.52	2.65	2.58
	5	13.70	13.80	2.67			2.72	2.68
5		14.98	15.05	2.66		2.64	2.72	2.63
		Average:		**2.665 Å**	2.69 Å	2.62 Å	2.71 Å	2.65 Å

The quantitative comparison of measured and calculated positions of maxima and minima is given in table 1, the value of *b* being given for each measured value of $4\pi \sin \frac{\theta}{2}/\lambda$ for Models *B*, *C*, *D*, *E* and *F*, except when the nature of the calculated curve prevents a comparison, as for Curve *B* beyond the third minimum. The second minimum is not used, as it is difficult to measure accurately. Of these, the values for Model *D* are to be accepted, the others being included to indicate limits of error due to uncertainty in the model. The consistency of the *b* values is satisfactory, the high and low values for the third and fourth maxima being due to the St. John effect. Averaged values for *b* are given in the bottom rows of the table. From these we conclude that the formic acid dimer has the hydrogen-bond structure, with resonating double bonds in the carboxyl groups, the O–H–O distance being 2.67 ± 0.04 Å, the C–O distance 1.29 ± 0.02 Å and the bond angle 125° ± 5°.

The value found for the O–H–O distance, 2.67 Å, is intermediate between the value in ice, 2.77 Å, and that in potassium dihydrogen phosphate, 2.54 Å. This indicates that with respect to the strength of the hydrogen bond the double molecules of formic acid are intermediate between these two crystals.

In this case resonance has no pronounced effect on the bond angle, the value of 125° found for the carboxyl group being that expected between a double and a single bond for a tetrahedral carbon atom.

The C–O distance of 1.29 Å is about equal to the distance for a double bond, with some indication, however, that complete resonance of a double and a single bond does not quite reduce each to the double-bond distance. (It may be mentioned that there is some evidence that the double-bond

radii given in Ref. 1 are about 2% too large, and that the double-bond carbon–oxygen distance should be 1.26 Å.) The only other available value for the carboxyl group, aside from the value 1.29 ± 0.05 Å reported in the following paper for the acetate group, is C–O = 1.25 ± 0.05 Å for crystalline oxalic acid dihydrate.[7] It seems probable that this value is slightly low, especially since the value 1.59 ± 0.07 Å reported for the bond between the two carboxyl carbon atoms is about 0.10 Å higher than the value expected for a single carbon-carbon bond serving as the path of conjugation for two double bonds. Moreover, it seems probable that the value C–O = 1.24–1.27 Å reported for the carbonate ion in various crystals is somewhat low, inasmuch as the distance for resonance of one double and two single bonds would be expected to be somewhat larger than that for one double and one single bond, as in the carboxyl group. An accurate redetermination of the parameter for these crystals should be made.

We are indebted to Dr. S. Weinbaum for many of the calculations involved in this investigation.

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[2] L. Pauling and J. Sherman, *J. Chem. Phys.*, **1**, 606 (1933).
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[6] W. M. Latimer and W. H. Rodebush, *Jour. Am. Chem. Soc.*, **42**, 1419 (1920).
[7] W. H. Zachariasen, Abstract of paper presented at Washington meeting of the American Physical Society, April 27, 1934.

THE STRUCTURE OF THE CARBOXYL GROUP. II. THE CRYSTAL STRUCTURE OF BASIC BERYLLIUM ACETATE

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The crystal structure of basic beryllium acetate, $Be_4O(CH_3COO)_6$, has been studied by Bragg and Morgan,[1] who reported some spectrometric intensity measurements and showed the cubic unit of structure to have $a_0 = 15.72$ Å and to contain eight molecules, and by Morgan and Astbury,[2] who showed the space group to be T_h^4. In neither study was the atomic arrangement determined. We have found an atomic arrangement which accounts satisfactorily for the data of these authors and for additional intensity data obtained photographically, and which provides information regarding the structure of the acetate group.